



# A novel three-dimensional manganese dioxide electrode for high performance supercapacitors



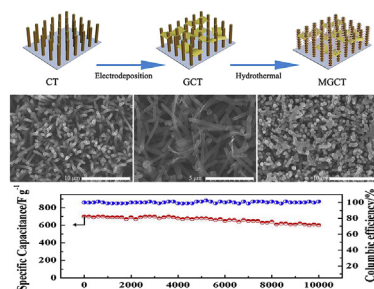
Shuying Kong, Kui Cheng<sup>\*\*</sup>, Yinyi Gao, Tian Ouyang, Ke Ye, Guiling Wang, Dianxue Cao<sup>\*</sup>

Key Laboratory of Superlight Material and Surface Technology of Ministry of Education, College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

## HIGHLIGHTS

- A 3D electrode with graphene nanosheet decorated on C/TiC nanowire array is built.
- MnO<sub>2</sub> nanoflakes uniformly grow on the 3D electrode via a simple hydrothermal method.
- The 3D MnO<sub>2</sub> nanoflakes electrode exhibits high electrochemical performance.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 16 October 2015

Received in revised form

22 December 2015

Accepted 20 January 2016

Available online 30 January 2016

### Keywords:

Manganese dioxide

Nanowire array

Graphene

Hydrothermal

Supercapacitor

## ABSTRACT

Development of MnO<sub>2</sub> based electrode materials for supercapacitor application with high comprehensive electrochemical performance, such as high capacitance, superior reversibility, excellent stability, and good rate capability, is still a tremendous challenge. In this work, a distinctive interwoven three-dimensional (3D) structure electrode with ultra-thin 2D graphene nanosheet decorated on the surface of 1D C/TiC nanowire array is built as the support to immobilize MnO<sub>2</sub> nanoflakes (MnO<sub>2</sub>-Graphene nanosheet-C/TiC nanowire array, denoted as MGCT). Compared with the normal 1D core/shell structure, this novel 3D architecture can dramatically not only increase the surface area for MnO<sub>2</sub> loading but also facilitate the ion and electron transfer. The electrochemical performance of the as-prepared 3D MnO<sub>2</sub> electrode is evaluated by cyclic voltammetry, galvanostatic charging-discharging tests and electrochemical impedance spectroscopy, high specific capacitance (856 F g<sup>-1</sup> at 2 A g<sup>-1</sup>), good rate capability (69.1% capacitance retention at 40 A g<sup>-1</sup> vs 2 A g<sup>-1</sup>), superior reversibility, and cycling stability (85.7% capacitance retention after 10,000 cycles at 10 A g<sup>-1</sup>) are obtained, suggesting that this novel structure can offer a new and appropriate idea for obtaining high-performance supercapacitor electrode materials.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

With the growing fossil consumption and environmental problems, the development of renewable energy sources has attracted attention from scientific and technological researchers. Efficient energy storage systems are needed to make the best use of the electricity generated from those intermittent renewable

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [chengkui@hrbeu.edu.cn](mailto:chengkui@hrbeu.edu.cn) (K. Cheng), [caodianxue@hrbeu.edu.cn](mailto:caodianxue@hrbeu.edu.cn) (D. Cao).

sources. Therefore, the development of high-performance energy storage devices has come to the front. Supercapacitor, as a bridge to connect the battery and dielectric capacitor, is considered as a preferable candidate energy storage device due to its high power density, long cyclic stability and rapid charge/discharge rate [1–3]. Whereas, compared with battery, nothing but the energy density is the major issues that remain to be addressed to make the use of supercapacitor popular. Therefore, the pseudo-capacitor, which the capacitance comes from faradaic reactions at the electrode/electrolyte surface, have drawn much attention due to its notably higher specific capacitances than that of the electrical double-layer capacitor, whose capacitance arises from the charge separation at an electrode/electrolyte interface. To date, various redox-active transition-metal oxides, such as RuO<sub>2</sub> [4], MnO<sub>2</sub> [5], Co<sub>3</sub>O<sub>4</sub> [6], Ni(OH)<sub>2</sub> [7], have been endeavored as the electrode materials for pseudo-capacitors. Among them, MnO<sub>2</sub> is one of the most ideal candidates owing to its high theoretical capacity (1370 F g<sup>-1</sup>), wide operating potential window in mild electrolyte, nontoxicity, low cost, and natural abundance. Unfortunately, the low conductivity (10<sup>-5</sup>–10<sup>-6</sup> S cm<sup>-1</sup>) and a relatively small surface area of pristine MnO<sub>2</sub> often limits its charge-discharge rate and energy density in a particular application [8,9].

In order to improve the electrochemical performance of MnO<sub>2</sub>-based electrodes, two strategies have been proposed. One is to incorporate MnO<sub>2</sub> on highly conductive support materials with high surface area, such as carbon nanotubes [10], carbon spheres [11] and graphene [5], to enhance its electrical conductivity. As one of the most appealing carbon materials, graphene has been widely used as the supporting material for MnO<sub>2</sub> materials due to its extraordinarily high electrical conductivity, superior mechanical flexibility and high thermal and chemical stability [12–14]. Chen and co-worker [15] have reported that a hybrid compound, in which nanolamellas MnO<sub>2</sub> was stabilized on the surface of graphene, could be employed as the electrode materials with an ideal electrochemical performance for supercapacitor. The other one is to combine MnO<sub>2</sub> with one-dimensional (1D) metals or metal oxides nanowire array to form a core/shell array, which can make use of the advantages of both components and offer special properties through a reinforcement or modification of each other, and also provides more active sites for the Faradaic reactions and shortens the ion diffusion pathways [16–18]. For example, Fan's group [19] has built a smart electrode made of Co<sub>3</sub>O<sub>4</sub>/MnO<sub>2</sub> core/shell nanowire array, which exhibits excellent electrochemical performance. By comparison, the binder-free electrodes fabricated by self-growing 1D core/shell array architecture directly on current-collecting substrates show more advantages in terms of enhancing the power density (or rate capability) and cycling stability, because this unique structure not only has the ability to increase the contact area between the electrolyte and active material but also provide accessible channels that facilitates mass and charge transport. Although promising specific capacitances have been achieved through the above method, such as TiO<sub>2</sub>@MnO<sub>2</sub> [20], Zn<sub>2</sub>SnO<sub>4</sub>@MnO<sub>2</sub> [21], NiCo<sub>2</sub>S<sub>4</sub>@MnO<sub>2</sub> [22], however, MnO<sub>2</sub> with 1D core/shell nanostructure is still a challenging task due to its low electro-conductivity of core and shell materials, which will result in a not ideal rate performance. A key challenge in this direction is to build up a novel architecture, in which the interface/chemical distributions are homogeneous and a fast ion and electron transfer is guaranteed.

In the present work, we designed and prepared a special interwoven three-dimensional (3D) structure electrode by combining 1D nanowire and 2D nanosheet units through a facile chemical vapor deposition followed by one-step optimized electrodeposition and one-step hydrothermal method successively. Different from those reported 1D core/shell structure, this unique

3D architecture (Graphene-C/TiC, denoted as GCT) with ultra-thin 2D graphene film decorated on the surface of 1D C/TiC nanowire array (denoted as CT), which act as not only the skeleton but also the sacrificial template for MnO<sub>2</sub> nanoflakes uniformly immobilization. In addition, 1D C/TiC nanowire array is chosen as substrate for its high electrical conductivity and high mechanical strength coupled with high corrosion resistance and stability in acidic and alkaline environments, which is one important issue for the real application [23,24]. Therefore, this 3D architecture electrode has inherited the high electrochemical activity from the full utilization of MnO<sub>2</sub> nanoflakes, the high electronic conductivity from graphene and TiC, simultaneously. High specific capacitance (856 F g<sup>-1</sup> at 2 A g<sup>-1</sup>), good rate capability (69.1% capacitance retention at 40 A g<sup>-1</sup> vs. 2 A g<sup>-1</sup>), superior reversibility, and cycling stability (85.7% capacitance retention after 10,000 cycles at 10 A g<sup>-1</sup>) were obtained, suggesting that this structure has a promising future as a new concept in high-performance supercapacitor electrode.

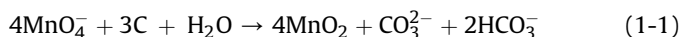
## 2. Experiment

### 2.1. Synthesis

**Synthesis of CT nanowire array electrode:** The C/TiC nanowire array was prepared via a chemical vapor deposition process [25] by using a piece of Ti6Al4V alloy as substrate and acetone as the carbon source. In brief, Ti6Al4V foils (10 × 10 × 1 mm<sup>3</sup>) were ultrasonically degreased in acetone and ethanol for 15 min sequentially, and then washed in deionized water. After that, Ti6Al4V foils were loaded onto a ceramic substrate and put it into in a horizontal tube furnace and heated 850 °C under an Ar atmosphere. Acetone was introduced into the chamber at a flow rate of 150 sccm with Ar as the carrier gas and heated for 90 min. The samples were cooled down to room temperature under Ar to obtain the substrate.

**Synthesis of GTC electrode:** The graphene oxide was synthesized by using a modified Hummers method [26]. The freestanding crumpled graphene nanosheets on CT nanowire array were electrodeposited in a three-electrode system, with a Pt counter electrode and Ag/AgCl electrode reference electrode. The electrolyte solutions consisted of 0.2 mg mL<sup>-1</sup> graphene oxide aqueous suspension and 0.1 M Na<sub>2</sub>HPO<sub>4</sub>. The deposition was performed by applying a constant current of -1 mA cm<sup>-2</sup> and lasted for different time (15, 30, 60 and 90 min) at room temperature. During the electrodeposition process, graphene oxide nanosheets were reduced into conductive graphene as reported in the literature [27] and synchronously deposited on the nanowire array surface. After electrodeposition, the electrode was washed with deionized water to remove the residual graphene oxide adsorbed on the electrode.

**Synthesis of MGTC electrode:** Synthesis of MGTC is enlightened by that MnO<sub>2</sub> can be produced by a reduction reaction between KMnO<sub>4</sub> and graphitic carbon [19], as followed:



Therefore, we have extended this reaction to an in-situ chemical redox reaction by using carbon shell of the CT nanowire array, and also the graphene nanosheet as carbon source, which confines the MnO<sub>2</sub> growth reaction specifically to the carbon surface, giving rise to a smart 3D structure. The hydrothermal process is as followed: the pristine GTC electrode prepared at different electrodeposition time was first immersed in 20 mL of 0.01 mol L<sup>-1</sup> KMnO<sub>4</sub> solution, then transferred to a 25 mL Teflon-lined autoclave and heated in an oven to 100 °C for 5 h. After the hydrothermal reaction, the obtained samples were washed with deionized water for several times and dried in air to obtain the final MGTC electrodes.

Download English Version:

<https://daneshyari.com/en/article/1285562>

Download Persian Version:

<https://daneshyari.com/article/1285562>

[Daneshyari.com](https://daneshyari.com)